CHEMICAL & PHARMACEUTICAL BULLETIN

Vol. 34, No.2 February 1986

Regular Articles

Chem. Pharm. Bull.
34(2) 445—449 (1986)

Pd(II) Ion Fixed on Sulfonated Polystyrene-Type Resin Catalysts for the Oxidation of 2-Methylnaphthalene to 2-Methyl-1,4-naphthoquinone with Hydrogen Peroxide

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(Received April 30, 1985)

The oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone (vitamin K_3) was carried out with aqueous (60%) H_2O_2 in acetic acid in the presence of Pd(II) salts at 50 °C. The activities of Pd(II) salts were in the order of $SO_4^{2-} > ClO_4^- > NO_3^- > AcO^- > PO_4^{3-} > Cl^- > Br^- > I^-$. The Pd(II) salts such as $PdSO_4$, $Pd(ClO_4)_2$, $Pd(AcO)_2$, and $PdCl_2$ were heterogenized by ion exchange between Pd(II) ion and protons of sulfonated polystyrene-type resin (SP resin) to give Pd(II)–SP resin. The use of 0.24% Pd(II)–SP resins gave a good yield (50 to 60%) of vitamin K_3 at 50 °C. The catalyst could be recovered by filtration and reused conveniently.

Keywords——oxidation; hydrogen peroxide; palladium catalyst; 2-methylnaphthalene; 2-methyl-1,4-naphthoquinone; vitamin K_3; sulfonated polystyrene-type resin

2-Methyl-1,4-naphthoquinone (vitamin K_3, VK_3) has been produced by the oxidation of 2-methylnaphthalene (2-MN) with chromic acid in 38 to 42% yields.[1)] In the presence of a crown ether (18-crown-6) a 62% yield has been achieved.[2)] However, the use of chromic acid as oxidizing agent is undesirable since laborious treatment of the waste water is necessary. Though the use of H_2O_2 in the presence of acid catalysts in place of chromic acid has been claimed in patents, drawbacks were the use of a large amount of HCl (60% yield)[3)] or a lower selectivity (38%).[4,5)] A recent investigation revealed that various aromatic hydrocarbons such as naphthalenes, anthracene, phenanthrene, durenes, and several alcohols have been oxidized with ammonium persulfate in the presence of cerium(IV) ammonium sulfate and silver(I) nitrate by forming a redox catalyst system in an emulsified cyclohexene–H_2O solvent; Ce(III) ions formed during the oxidation are converted immediately to Ce(IV) ions with ammonium persulfate in the presence of Ag(I) ions. By using this catalyst system, 2-MN has been oxidized to give a mixture of VK_3 in 60% yield and 6-methyl-1,4-naphthoquinone in 20% yield.[6)] As has been briefly reported,[7)] we studied the oxidation of 2-MN to VK_3 and found that Pd(II) ion fixed on sulfonated polystyrene-type resin (Pd(II)–SP resin) showed good activity and selectivity. 2-MN was oxidized with H_2O_2 (60 %) in acetic acid at 50 °C to give 50 to 60% yields of VK_3. The yields were affected by the properties of SP resins used as the support for palladium and by the reaction conditions, such as the reaction temperature,[7)] the concentration of H_2O_2, and solvents. During the investigation, we observed that the amount of palladium fixed on SP resin significantly affected the yield of VK_3.

This report deals with a novel catalyst system for the oxidation of 2-MN to VK_3 with aqueous H_2O_2 and with the properties of palladium catalysts. The catalysts were recovered and recycled to give VK_3 in 50 to 60% yields.

Experimental

Reagents and Preparation of the Catalysts——Metal acetates, H_2PtCl_6, metal chlorides, $Pd(NO_3)_2$ (Wako Pure Chemical Industries), aqueous 30% H_2O_2 (Hayashi Pure Chemical), and SP resins (50w-×2, ×4, ×8, ×12) (Dow Chemical) were purchased commercially. $PdSO_4$, $Pd(ClO_4)_2$, $Pd_3(PO_4)_2$, $PdBr_2$, and PdI_2 were prepared *in situ* from $Pd(AcO)_2$ and the corresponding mineral acids in acetic acid. Aqueous 60% H_2O_2 was obtained from Mitsubishi Gas Chemical. The conditioning of SP resin (50w-×8, 1 g, H form, water content 50%) was carried out by allowing it to stand for 1 h in 30 ml of acetic acid. The solvent was removed, and Pd(II)–SP resin catalysts were prepared from $Pd(AcO)_2$ and SP resin by stirring in 10 ml of acetic acid for 5 h at 50 °C. The catalyst was separated and washed with acetic acid.

General Procedure for the Oxidation of 2-MN——2-MN (0.35 g, 2.5 mmol), acetic acid (10 ml), and the catalyst were added to a 50 ml flask. The oxidation was started by the addition of 60% H_2O_2 (0.35 ml, 7.8 mmol) under magnetic stirring at 50 °C. After almost all the H_2O_2 had been consumed (4 h), 0.35 ml of 60% H_2O_2 was added and the solution was heated for 4 h. The products were analyzed by high-performance liquid chromatography (HPLC) (M & S pack C 18, 4.6 × 150 mm column, Gilson Co., model 302) using $MeOH-H_2O$ (100 : 15) as the eluent (flow rate, 0.5 ml/min; detector, ultraviolet (UV) at 285 nm) with 2,6-dimethylnaphthalene (DMN) as an internal standard. Retention times were VK_3, 5.9 min; 2-MN, 10.2 min; and DMN, 14.1 min. After the reaction, the catalyst was recovered by filtration and VK_3 was separated by the addition of water (four times the volume) to the filtrate. VK_3 that remained in the filtrate was extracted with hexane. Evaporation of the solvent gave crude VK_3 as yellow crystals.

Results and Discussion

Preliminary Catalyst Screening in a Homogeneous System

The activity of metal acetates or chlorides was studied in the oxidation of 2-MN with 30% H_2O_2 in acetic acid. Reaction temperatures lower than 40 °C retarded the oxidation considerably. Above 60 °C, fast oxidation took place even in the absence of catalysts, with poor selectivity. Therefore, we employed the reaction temperature of 45 °C. The results are shown in Table I.

Among acetates, $Pd(AcO)_2$ gave the highest yield (5.7%) of VK_3, followed by H_2PtCl_6 (a 3.1% yield). On the other hand, poor activities were obtained with the acetates of Fe, Co, Ni, Cu, Zn, and Ag, though these compounds are commonly used in the oxidation of various organic compounds. The chlorides of Os, Au, Ir, Ni, and Co also gave VK_3 in yields of between 2.6 and 0.1%.

TABLE I. Screening of Metal Ions as Catalysts in the Oxidation of 2-MN to VK_3 with H_2O_2 (30%)

Run	Catalyst (mg)	Yield (%)	Run	Catalyst (mg)	Yield (%)
1	$Pd(AcO)_2$ (10)	5.7	8	$H_2PtCl_6 \cdot 6H_2O$ (10)	3.1
2	$Fe(AcO)_2(OH)$ (10)	2.6	9	$OsCl_3 \cdot 3H_2O$ (10)	2.6
3	$Cu(AcO)_2 \cdot H_2O$ (20)	1.6	10	$HAuCl_4 \cdot 4H_2O$ (10)	1.4
4	$Co(AcO)_2 \cdot 4H_2O$ (20)	1.5	11	$IrCl_3$ (10)	1.2
5	$Zn(AcO)_2 \cdot 2H_2O$ (10)	1.0	12	$NiCl_2 \cdot 6H_2O$ (20)	0.3
6	Ag(AcO) (10)	0.4	13	$CoCl_2 \cdot 6H_2O$ (20)	0.1
7	$Ni(AcO)_2 \cdot 4H_2O$ (20)	0.3			

2-MN 0.35 g (2.5 mmol), 30% H_2O_2 0.7 ml (6.8 mmol), and AcOH 5 ml were used. The oxidation was carried out at 45 °C for 4 h.

TABLE II. Effect of Anions of Pd Salts in the Oxidation of 2-MN to VK_3 with H_2O_2 (30%)

Run	Anion	Initial rate	
		2-MN ($\times 10^{-3}$ mmol/min)[a]	VK_3 ($\times 10^{-3}$ mmol/min)
1	SO_4^{2-}	6.4	2.4
2	ClO_4^-	6.1	2.2
3	NO_3^-	5.2	1.7
4	AcO^-	1.9	0.6
5	PO_4^{3-}	1.8	0.4
6	Cl^-	2.1	0.5
7	Br^-	1.2	0.4
8	I^-	0.9	0.4

2-MN 0.35 g (2.5 mmol), 30% H_2O_2 0.7 ml (6.8 mmol), and AcOH 5 ml were used. The oxidation was carried out at 45 °C. *a*) The rate of decrease of 2-MN.

TABLE III. Oxidation of 2-MN with H_2O_2 in the Presence of Palladium Catalysts

Catalyst (g)	Temp. (°C)	Size (mesh)	H_2O_2 (ml)	Conv. (%)	Yield (%)	Select. (%)
No catalyst	50		60%, 0.7	20.1	7.8	38.5
$Pd(AcO)_2$ (0.005)	50		60%, 0.7	59.1	28.4	48.0
SP × 8[a] (1.0)	50	200—400	60%, 0.7	54.9	20.6	37.5
0.24% Pd-SP × 2[b] (1.0)	50	200—400	60%, 0.7	98.3	51.4	52.3
0.24% Pd-SP × 4[c] (1.0)	50	200—400	60%, 0.7	97.1	50.0	51.5
0.24% Pd-SP × 8 (1.0)	40	200—400	60%, 0.7	79.9	41.5	51.9
0.24% Pd-SP × 8[d] (1.0)	50	200—400	60%, 0.7	90.6	51.8	57.2
0.24% Pd-SP × 8[e] (1.0)	50	200—400	60%, 0.7	90.7	51.1	56.3
0.24% Pd-SP × 8[f] (1.0)	50	200—400	60%, 0.7	50.0	27.9	55.8
0.24% Pd-SP × 8 (1.0)	50	200—400	60%, 0.7	97.2	54.2	55.8
0.24% Pd-SP × 8 (1.0)	50	200—400	30%, 1.4	88.8	41.6	46.9
0.24% Pd-SP × 12[g] (3.0)	50	100—200	60%, 0.7	89.7	59.4	66.2
0.24% Pd-SP × 12 (1.0)	50	100—200	60%, 0.7	46.7	25.3	54.2

2-MN 0.35 g (2.5 mmol) and AcOH 10 ml were used. The oxidation was carried out for 8 h. *a*) DOWEX 50W-×8 (an 8% divinylbenzene type, water content 50%) was used. *b*) DOWEX 50W-×2 (a 2% divinylbenzene type, water content 75%) was used. *c*) DOWEX 50W-×4 (a 4% divinylbenzene type, water content 65%) was used. *d*) The ion-exchanged catalyst was prepared from $PdSO_4$ and SP resin (DOWEX 50W-×8). *e*) The ion-exchanged catalyst was prepared from $Pd(ClO_4)_2$ and SP resin (DOWEX 50W-×8). *f*) The ion-exchanged catalyst was prepared from $PdCl_2$ and SP resin (DOWEX 50W-×8). *g*) DOWEX 50W-×12 (a 12% divinylbenzene type, water content 33%) was used. Other ion-exchanged catalysts were prepared from $Pd(AcO)_2$ and SP resins.

Anions of palladium salts affected the oxidation rate of 2-MN (Table II). The oxidation rates in the presence of $PdSO_4$ or $Pd(ClO_4)_2$ were five to six times faster than that with PdI_2.

The order of activity of Pd(II) salts suggests that the oxidation proceeds by forming palladium complexes; the rates depend upon the strength of the coordination of anions to the central metal ions, and the order is $SO_4^{2-} > NO_3^- > RCO_2^- > Cl^- > Br^- > I^-$.[8]

Effect of the Amount of Pd(II) Ion Fixed on SP Resin

From the practical standpoint, a solid catalyst is desirable for the easy separation of the catalyst from the reactants. In the preparation of oxidizing catalysts, SP resin, an organic polymer carring sulfonic acid moieties, was used as a support for palladium, since $PdSO_4$ was the most efficient catalyst for the oxidation of 2-MN in a homogeneous system. Table III shows that the ion-exchanged Pd(II)–SP resin catalysts prepared from SP resin and such Pd(II) salts as $Pd(AcO)_2$, $PdSO_4$, and $Pd(ClO_4)_2$ gave good VK_3 yields of 50—55% at 50 °C. On the other hand, a poor activity was obtained with the catalyst prepared from $PdCl_2$ and SP resin.

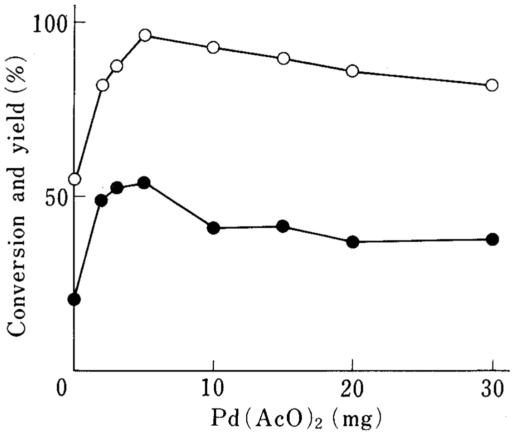

Fig. 1. Effect of the Amount of Pd(II) on Sulfonated Polystyrene Type Resin in the Oxidation of 2-MN to VK_3 with H_2O_2 (60%)

2-MN 0.35 g (2.5 mmol), 60% H_2O_2 0.7 ml (15.6 mmol), Pd(II)–SP resin (DOWEX 50w-×8, 200—400 mesh) 1 g, and AcOH 10 ml were used. The oxidation was carried out at 50 °C for 10 h. ○, conversion, ●, yield.

TABLE IV. Repetitive Usage of Catalyst Recovered by Filtration in the Oxidation of 2-MN to VK_3 with H_2O_2 (60%)

Run	Yield (%)
1	60.2
2	55.4
3	51.7
4	50.5

2-MN 3.5 g (25 mmol), 60% H_2O_2 7 ml (156 mmol), 0.24% Pd(II)–SP resin (DOWEX 50W-×8, 200—400 mesh) 10 g, and AcOH 50 ml were used. The oxidation was carried out at 50 °C for 10 h.

The oxidation of 2-MN was carried out with various Pd(II) ion-exchanged catalysts. As shown in Fig. 1, maximum yield was obtained when a small amount of $Pd(AcO)_2$ (5 mg, 0.022 mmol) was ion-exchanged on SP resin (1 g, acidity 2.40 mmol/g). Therefore, the ratio of Pd(II) ions to the acid sites of SP resin is around one-hundredth.

On the other hand, a 4.8% Pd(II)–SP resin catalyst prepared from $Pd(AcO)_2$ (100 mg) and SP resin (1 g) decomposed H_2O_2 vigorously. Unexpectedly, the selectivity in the presence of the Pd(II)–SP resin was higher than that in the homogeneous system of Pd(II) salts. These results suggest that the coordination of 2-MN to palladium in the matrix of SP resin might have regulated the orientation with respect to the 1 and 4 position of 2-MN. If Pd(II) ions were distributed homogeneously throughout the resin, the selectivity for VK_3 might be close to that obtained by the oxidation in the presence of SP resin itself. Therefore, as a model for Pd(II)–SP resin, a particle of the resin covered with a thin palladium layer may be considered. For 0.24% Pd(II)–SP resin catalyst, the palladium layer would be spread over the surface of the resin to a thickness of one three-hundred and twentieth of its radius.[9]

Effect of the Physical Properties of SP Resins as Supports

The oxidation of 2-MN using SP resins with different cross-linking ratios was studied (Table III). All the SP resins examined (2—12% divinylbenzene types) gave good selectivities for VK_3 in the first run. On the other hand, lower cross-linked SP resins (2 and 4% divinylbenzene type) collapsed during three cycles of the oxidation. Therefore, we used 8 and 12% divinylbenzene-type SP resins as the supports.

The size of SP resin particles also affected the yield and the selectivity for VK_3. Though resin of large particle size (100—200 mesh) is convenient in the handling and separation procedures, both the conversion and the selectivity were lower than those of a smaller size (200—400 mesh) resin when the activity was compared at the same palladium content and catalyst weight.

Oxidizing Agents and Reaction Conditions

As for other oxidizing agents, neither oxygen nor *tert*-butylhydroperoxide oxidized 2-MN on the Pd(II)–SP resin catalyst. Hydrogen peroxide in acetic acid was the only agent to give VK_3. In acetic acid, a higher concentration (60%) of H_2O_2 gave a good selectivity of 55.8% for VK_3 compared with a value of 46.9% with 30% H_2O_2. Such carboxylic acids as formic, propionic, chloroacetic, and fluoroacetic acids were good solvents for this oxidation. Increase in the acid strength of the solvents increased the oxidation rates. On the other hand, alcohols, dioxane, acetonitrile, dimethylformamide, dimethylsulfoxide, or hexamethylphosphoramide completely suppressed the oxidation. From these results, the active species for the oxidation of VK_3 was supposed to be peracetic acid produced from acetic acid and H_2O_2. The addition of H_2O_2 at once decreased the selectivity to 45%. Therefore, H_2O_2 was added separately in two portions or added dropwise.

Repetitive Usage of Catalyst

A catalyst of 0.24% Pd(II)–SP resin was prepared and 2-MN (3.5 g) was oxidized with 60% H_2O_2 (7 ml) repeatedly using the recovered catalyst. The results are shown in Table IV. H_2O_2 was added dropwise during 4 h at 50 °C and the oxidation was continued for a further 6 h. When the conversion reached 95% (after 10 h), the catalyst was separated by filtration. The oxidation was carried out again using the recovered catalyst with fresh addition of 2-MN, H_2O_2, and acetic acid. Four cycles were successively carried out in 60 to 50% yields.

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9) This value was calculated from the mean diameter of resin beads (1.62×10^{-2} cm), the specific gravity of the resin (1.28 g/cm^3), the acidity (2.40 mmol/g), and the $Pd(AcO)_2$ content (2.23×10^{-2} mmol), according to the equation

$$\frac{4/3\pi r^3-4/3\pi(r-a)^3}{4/3\pi r^3}=\frac{2.23\times10^{-2}}{2.40}$$

where

r: mean radius of resin beads
a: thickness of palladium-exchanged layer.